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REDUCED GRAIN BOUNDARY MOBILITY AND THE SINTERING OF  
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REDUCED GRAIN BOUNDARY MOBILITY AND  
THE SINTERING OF MOLYBDENUM

FINAL REPORT

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U.S. ARMY RESEARCH OFFICE

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## ABSTRACT

The sintering of a refractory metal like molybdenum requires a high temperature which can cause rapid grain growth, pore isolation and poor sintered properties. An analysis has been performed of the sintering behavior to isolate specific actions which will aid sintering and retard grain growth. This analysis has led to a Mo-Ni-SiO<sub>2</sub> composition which experimentally exhibits high sinterability and a fine grain size. The nickel addition acts as a sintering activator, giving high interfacial diffusion rates for molybdenum. Alternatively, the silica is added as a fine dispersoid to provide a drag force on migrating grain boundaries. Both isothermal and constant heating rate experiments have been used to isolate the nickel and silica effects on sintering kinetics. In addition, samples have been fully densified by hot isostatic pressing. The as-pressed microstructures further demonstrate the attributes of the new composition. Prolonged annealing at temperatures up to 1350°C evidenced a stable, fine grain size microstructure. Other experiments and analysis have been performed to better define activated sintering and to help develop a better theory.

## STATEMENT OF THE PROBLEM

The processing of crystalline powders relies on obtaining densification during the sintering cycle. The latter stages of sintering play a dominate role in determining final compact properties. Theories which exist for the latter stages have assumed an idealized grain growth rate and have ignored various retarding effects like porosity. Consequently, these theories fail to explain most data, especially that developed under conditions of sintering enhancement. The role of grain boundaries on sintering densification



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has been observed for many years. It is postulated that control of grain boundary mobility is a route to higher sintering rates and improved properties, especially in combination with sintering activators. In this study, the latter sintering stages are viewed as competitive processes involving densification, pore rounding and grain growth. This concept provides a basis for new theories and experiments aimed at unifying our understanding of sintering and its critical dependence on the grain boundary mobility. Inclusion of grain boundary mobility into densification rate equations is the basis for demonstrating various sintering enhancement treatments for molybdenum. Consequently, focus is given to both enhanced sintering treatments using diffusion activators like palladium, nickel and platinum, and grain boundary pinning agents like inert dispersoids of silica. Experimental evidence for the success of this idea is obtained from constant heating rate dilatometry, isothermal sintering and hot isostatic pressing.

#### SUMMARY OF IMPORTANT RESULTS

Molybdenum is prepared by powder metallurgy techniques for several applications. Consequently, there is a reasonable amount of data available on processing. The properties of molybdenum are highly dependent on the processing cycle and powder characteristics. The addition of selected transition metals like nickel greatly increases the sintering rate but also increases the grain coarsening rate. The focus of both the theoretical and experimental efforts during this research have been on microstructure control during sintering of molybdenum. Enhanced sintering treatments have been used to aid densification and dispersoids have been used to retard grain growth and pore coalescence. Theoretical developments have progressed in parallel to these experimental efforts. Below are summarized the major

results of this research.

The sintering process during intermediate stage sintering of molybdenum is viewed as a competition between densification, grain growth and pore rounding events. From a practical viewpoint it is most desirable to enhance densification while suppressing pore rounding and grain growth. To examine this problem, a mathematical model was constructed with a view towards enhanced sintering. Specific attention was given to interfacial segregation effects on grain growth and sintering; segregated solutes change the boundary cohesive energy, diffusivity and mobility. Analysis was focused on solutes which segregate to boundaries, increase the cohesive energy, lower the boundary mobility while providing high diffusivity transport paths. From this theoretical analysis it was shown that diffusivity to mobility ratios over approximately  $2 \times 10^9 \text{ N/m}^3$  lead to enhanced sintering densification for molybdenum.

One means of increasing the diffusivity for molybdenum is through addition of latter transition metals. Early study was given to both the effect of different molybdenum powder types, impurities and activators. Isothermal sintering was conducted at temperatures up to  $1150^\circ\text{C}$ , using two powders treated with activators of nickel, palladium or platinum. It was found that molybdenum powder derived from molybdenum trioxide had a higher impurity level which aided final stage densification. However, this impurity level decreased the initial sintering rate. The role appears to be associated with decreased dislocation motion initially and subsequent slower rates of grain growth. Additives like nickel increase the sintering rate at these low sintering temperatures. This effect is due to enhanced diffusion through grain boundaries rich in the chemical additives. It is significant that the long term benefits associated with impurities (grain boundary drag) are present in molybdenum processed by enhanced sintering.

During this research major focus has been given to activated sintering. A secondary emphasis has been placed on liquid phase sintering. Activated sintering refers to a class of techniques designed to lower the thermal activation energy barrier associated with sintering. The benefits of activated sintering include lower sintering temperatures, shorter sintering times and improved properties. Enhanced diffusion during sintering is possible with appropriate selection of an activator addition. The identification of an appropriate sintering aid is based on phase diagram features. Considerable progress has been made in identifying the features important to successful activated sintering. The enhanced diffusion process associated with activated sintering has been detailed in a quantitative theory (see attached list of publications). The concept relies on the electronic theories of Samsonov and Engel-Brewer. Enhanced sintering is treated as rapid diffusion through a segregated activator layer located at the interparticle layer located at the interparticle grain boundaries. The theory uses the Engel-Brewer model to predict diffusivities and geometric models to predict net rates of sintering. Experimental measurements on molybdenum doped with nickel show that the theory can only predict lower bound estimates on shrinkage. This is due in part to a failure to include plastic flow contributions in the model. In addition, the theory assumes a longer diffusion path length than may be necessary based on observed grain size changes. Consequently, modifications to the theory should provide good estimates of the sintering rate for refractory metal alloys.

From the various measurements it was observed that nickel increased the grain growth rate for molybdenum. Measurements on tungsten with activator additions showed grain growth to have a negative effect on mechanical properties. It is well known that grain boundaries act as effective vacancy sinks when densifying a powder compact. Accordingly, any change in the pore-grain boundary configuration, such as occurs with grain growth, significantly influences the

sintering process. Initially all the pores are located at the grain boundaries since the pores and grain boundaries are simultaneously formed at the interparticle contact region. In the initial stage of sintering, the large neck curvature prevents grain boundary migration. However, as the pores become rounded and shrink they become less effective at pinning the grain boundaries, and grain growth may occur. We have analyzed several geometries and conclude this is not a problem until 92% density is attained in molybdenum.

Grain growth can reduce the shrinkage rate in several ways. First, the increasing grain size results in a lower concentration of vacancy sinks. Second, grain growth may lead to grain boundary breakaway from the pores with an increase in the vacancy diffusion distance and therefore slower shrinkage rates. A pore may be dragged by a grain boundary depending on the pore and grain boundary mobilities and the driving force for grain growth. Since grain boundaries are fast diffusion paths, a pore which becomes isolated shrinks at a much slower rate. Finally, grain growth is a mechanism by which pores coalesce. Pore coalescence decreases the mean pore radius of curvature and thereby reduces the rate of vacancy emission.

During enhanced sintering, our data shows that grain growth can have a very negative effect. Model analysis for sintering molybdenum at approximately 92% density shows the positive effects of nickel and silica additions. Both constant heating rate and isothermal experiments evidence more intense sintering for molybdenum treated with 0.37 wt. % nickel and 0.02 wt. % silica. The sintering shrinkage of molybdenum is increased by a factor of ten at 1000°C due to the nickel addition. The shrinkage rate of nickel activated molybdenum is further increased by 67% with the silica additions. The sintered material exhibits a higher density and finer grain size due to



this treatment. Additionally, the nonisothermal processing appears to be beneficial over traditional isothermal sintering.

As a final examination, several molybdenum compositions were consolidated by hot isostatic pressing at 1300°C. The alloys included pure molybdenum, molybdenum activated with nickel, and two levels of silica in activated molybdenum. The as-consolidated materials containing nickel were 100% dense. Furthermore, the as-consolidated microstructures showed that silica had a positive effect on grain size. Isothermal anneals were conducted on these compacts at temperatures ranging up to 1350°C, for times of several days. The silica dispersion proved highly effective in maintaining a fine grain size.

Thus this research has demonstrated that various agents can be added to molybdenum to control the sintering and microstructure. The grain boundary mobility has an important role in the later stages of sintering. Since grain boundaries are known to be effective vacancy sinks, densification can be enhanced through grain growth control. Initially, pores are at the grain boundaries but as they coalesce and shrink during sintering they become less effective as grain boundary pinning agents. When the grain boundaries break away from the pore structure, the densification rate decreases.

Various techniques exist to control grain growth. These include solute segregation, particle size distribution control, dispersoid drag, and nonisothermal sintering.

Activated and liquid phase sintering are examples of a solute segregating to the grain boundaries. This method shifts the diffusivity/mobility ratio to favor rapid densification. There are critical mobilities below which dispersoids are dragged by moving boundaries. Experimental observations on the effects of dispersoids evidence that both grain size and densification can be altered by such inclusions. By keeping the boundary mobility sufficiently low, through

temperature control, higher endpoint densities can be produced by dispersoid drag.

Since grain boundary mobility is highly sensitive to the sintering temperature, it is therefore possible to enhance densification through temperature control. Nonisothermal sintering provides a means of controlling the grain boundary mobility to optimize shrinkage. This interpretation correlates with the observed finer grain sizes and higher endpoint densities produced in this research. Thus grain boundary mobility provides a basis for creating a predictive model for rate controlled sintering.

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